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Possibility of using tetrafluorohydrazine as an oxidiser in a supersonic cw chemical HF laser

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Abstract. **We report a computational and experimental study of the possibility of replacing NF_3 nitrogen trifluoride, which is used in the NF_3–D_2–He fuel composition in the atomic fluorine generator of a supersonic cw chemical HF laser, with N_2F_4 tetrafluorohydrazine. As a result of comparing the specific energy characteristics of an HF laser operating with each of the oxidisers, it is shown that the replacement of nitrogen trifluoride with tetrafluorohydrazine in the same laser model leads to an increase in the specific energy output by 13%–15%. In this case, it is possible to reduce the specific mass of the oxidiser storage system (the ratio of the mass of the oxidiser storage system to the laser facility power), reduce the oxidiser tank dimensions, and simplify the active medium generator design by eliminating the ignition system of the NF_3 oxidiser with a D_2 primary fuel.**

Keywords: *supersonic cw chemical HF laser, oxidiser, tetrafluorohydrazine, nitrogen trifluoride, specific energy and mass-dimensional characteristics.*

1. Introduction

In recent years, there has been an increased interest in the practical application of laser technology in space [1–3]. Thus, Avdeev et al. [4, 5] substantiated the possibility of cleaning the near-Earth space from fragments of space debris by a laser facility based on a high-power supersonic cw chemical HF laser (HF-CWCL). The requirements for the facility characteristics have been determined, including the laser radiation power and divergence, the pulse duration and repetition rate when operating in a repetitively pulsed regime, the duration of laser irradiation of space debris fragments to ensure their removal from the orbit of the spacecraft being protected.

The scope of engineering problems solved with such a laser facility in the orbit largely depends on the supply of fuel components necessary for the HF-CWCL operation aboard a spacecraft. In this regard, two important factors are of particular importance: the energy efficiency of the fuel used in the atomic fluorine generator (its specific energy output $N_\Sigma = N/m_\Sigma$, where N is the laser radiation power and m_Σ is the total mass fuel consumption), which determines the mass and size characteristics of the laser facility, and its manufacturability, which affects the operational characteristics of the fuel.

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For high-power HF-CWCLs, the fuel with the use of NF_3: NF_3–D_2–He nitrogen trifluoride as an oxidiser is currently recognised as the most effective according to the energy–manufacturability criterion [6]. However, this fuel is also not free from certain shortcomings. First, nitrogen trifluoride is usually stored in a gaseous state at a high (up to 15 MPa) pressure, which degrades the mass characteristics of the storage system. On the other hand, the storage of NF_3 in the liquid state requires, due to its cryogenic nature, special means, which significantly complicates the laser system. Secondly, the absence of self-ignition of nitrogen trifluoride upon contact with known primary fuels requires the use of a special ignition system (chemical or electroplasmic), which complicates the design of the active medium generator. And thirdly, the specific energy consumption of the NF_3–D_2–He fuel is not the highest. Replacing nitrogen trifluoride with a more energy-efficient oxidiser, such as N_2F_4 tetrafluorohydrazine, can lead to the production of a new fuel with an increased specific energy output [7].

Theoretically, tetrafluorohydrazine is considered as a promising rocket fuel oxidiser [8, 9]. Information about the practical use of N_2F_4 in laser technology is extremely limited. This circumstance became the basis for conducting a computational and experimental study on the possibility of using N_2F_4–D_2–He fuel for a HF-CWCL atomic fluorine generator.

2. Tetrafluorohydrazine as a chemical component

The N_2F_4 tetrafluorohydrazine is a representative of the class of nitrogen fluorides, a fluorine-containing analogue of N_2F_4 hydrazine, in which hydrogen atoms are replaced by fluorine atoms. It was synthesised relatively recently, in 1958 [10], and already in 1960 the United States launched its industrial production by the conversion of nitrogen trifluoride over coal according to the reaction $2NF_3 + 0.5C \rightarrow N_2F_4 + 0.5CF_4$.

The physicochemical properties of tetrafluorohydrazine are given in [11]. For performance evaluation, it is essential that under normal conditions N_2F_4 is a colourless gas with a characteristic smell similar to that of fluorine. Its critical temperature is 309 K, the critical pressure is 7.7 MPa, and its performance properties are very close to fluorine, i.e. it is toxic and chemically aggressive. It is a strong oxidiser. It has a satisfactory thermal stability and begins to decompose slowly when heated to a temperature of 423–473 K according to the reaction $N_2F_4 = (4/3)NF_3 + (1/3)N_2$.

In terms of energy parameters, tetrafluorohydrazine is somewhat inferior to fluorine, but has a relatively high boiling point (200 K) and a low solidification temperature (105 K), which facilitates its operation compared to other

fluorine-containing oxidisers. It can be stored in a liquid state at a temperature of 293 K and a relatively low overpressure, up to 2.5 MPa, without forced cooling [11]. In addition, N_2F_4 self-ignites upon contact with known primary fuels.

An important feature of the N_2F_4 molecule is its ability to equilibrium dissociation into NF_2 radicals according to the $N_2F_4 \leftrightarrow 2NF_2$ scheme, the degree of which depends on temperature and pressure. This feature allows us to consider tetrafluorohydrazine both as an N_2F_4 molecule and as an NF_2 radical. This dual structure is reflected in the chemical properties of tetrafluorohydrazine. The available experimental data show that N_2F_4 is capable of a dual chemical action – difluoroamination and fluorination, and besides, the fluorinating effect is associated with the manifestation of the N_2F_4 molecule's properties.

To dissociate the N_2F_4 molecule, it is necessary to break two types of bonds: N–N and N–F. According to work [11], the N–N bond breaking energy is 21.5 kcal mol^{-1}, while the average N–F bond breaking energy is 70.5 kcal mol^{-1}. In the NF_3 molecule, the breaking energy of the first bond (N–F), the second bond (NF–F), and the third bond (NF_2–F) is 55, 80, and 55 kcal mol^{-1}, respectively. Thus, the total energy costs for the dissociation of the NF_3 molecule significantly exceed those for the N_2F_4 molecule. Lower energy costs for the dissociation of the tetrafluorohydrazine molecule will obviously require smaller amounts of the oxidiser to produce equal amounts of atomic fluorine, which in turn will lead to an increase in the specific energy output N_Σ. The purpose of this paper is to find an answer to the question of how significant this increase can be.

It is clear that for an objective assessment of the comparative energy efficiency of various fuels, their comparison should be carried out with optimal chemical compositions that provide the maximum level of the specific energy output for each type of fuel. To determine such compositions, a special computational and experimental study was conducted in this work.

3. Computational conditions

To obtain sufficiently accurate results of numerical calculations of the HF-CWCL energy parameters, it is necessary to use the most complete gas-dynamic and kinetic mathematical models of the processes occurring in the gas-dynamic path elements. With this in mind, we used the following models developed at the Russian Scientific Centre 'Applied Chemistry': a two-dimensional model of a chemically equilibrium flow in the combustion chamber of an atomic fluorine generator, which takes into acount viscous effects and heat transfer in the narrow-channel approximation [12]; a two-dimensional model of the flow in the nozzle block's nozzles, which describes chemical nonequilibrium reactions in the gas phase and catalytic recombination of fluorine atoms on the nozzle walls with allowance for viscous effects and heat transfer on the walls and the impact of these effects on the inviscid flow in the boundary layer approximation [13]; and a two-dimensional model of the flow in a Fabry–Perot resonator, which describes chemical, vibrational and radiation kinetics with regard to viscous effects and convective transport on the basis of a system of equations for the dynamics of a multicomponent chemically reacting gas mixture in the narrow-channel approximation [14].

The output energy characteristics of the laser were determined by sequentially calculating the flow in individual elements of its gas-dynamic path using the above models. The laser characteristics were determined based on the condition of quasi-stationary lasing at individual vibrational–rotational transitions of the HF(v) molecule under the assumption that an equilibrium (Boltzmann) distribution over rotational levels exists at each vibrational–rotational level at the local translational temperature of the mixture. The spectral line broadening was assumed to be Doppler inhomogeneous, characteristic of gases at low pressures.

To determine the optimal chemical composition of fuels based on nitrogen trifluoride and tetrafluorohydrazine, two series of numerical parametric calculations were performed. In each series, the coefficients α and ψ determining the composition of fuels were varied, the conditional formulae of which were as follows:

$$D_2 + (2/3)\alpha NF_3 + [\psi(\alpha - 1) - \alpha/3]\ He + \alpha_2(\alpha - 1)H_2, \quad (1)$$

$$D_2 + (1/2)\alpha N_2F_4 + [\psi(\alpha - 1) - \alpha/2]\ He + \alpha_2(\alpha - 1)H_2. \quad (2)$$

Here, $\alpha = n_{F_2}/n_{D_2}$ is the coefficient of the oxidiser excess, determined by molecular fluorine; $\psi = n_{He} + n_{N_2}/(n_{F_2} - n_{D_2})$ is the total number of moles of diluent (helium and nitrogen) per mole of free fluorine in the composition of combustion products; $\alpha_2 = n_{H_2}/(n_{F_2} - n_{D_2})$ is the excess coefficient of the secondary fuel; and n_{H_2}, n_{F_2}, n_{D_2}, n_{He}, and n_{N_2} are the amounts of moles of hydrogen, fluorine, deuterium, helium, and nitrogen. Formulae (1) and (2) assume that nitrogen atoms in the composition of combustion products are contained only in free nitrogen molecules. This is confirmed by thermodynamic calculations, according to which the content of unstable radicals of NF and NF_2 type, and also the content of atoms of N and original molecules of NF_3 and N_2F_4 in the composition of combustion products is negligible (does not exceed tenths of a percent).

When performing numerical calculations, the coefficients of the oxidiser excess and fuel mixture dilution were varied in the following ranges: $\alpha = 1.3–2.0$, and $\psi = 5–20$. The secondary fuel excess coefficient α_2 was taken equal to 20. The absorption coefficients of the cavity mirrors were assumed to be 5%, which approximately corresponded to the real quality of the mirrors, and the output mirror transmittance was taken equal to zero (laser power was measured by the closed cavity method). The optical path length in the cavity was taken equal to 250 mm, as in the experimental bench model of the HF laser under study [15], and the pressure in the combustion chamber of the atomic fluorine generator was $p_c = 0.1$ MPa.

4. Experimental conditions

The experimental part of the study was carried out on a bench installation using the HF-CWCL model with an estimated power of 5 kW, equipped with a flat nozzle block corresponding to the nozzle–nozzle reagent mixing scheme [15]. The length of the atomic fluorine generator's combustion chamber (230 mm) was taken in accordance with the results of work [6] as an average between the lengths of the combustion chamber when operating the laser on fuels with the use of molecular fluorine (210 mm) and nitrogen trifluoride (250 mm). Tetrafluorohydrazine, synthesised at the pilot plant of at the Russian Scientific Centre 'Applied Chemistry', contained 92% of the main product's volume. All fuel components were in a gaseous state.

The experiments were carried out on fuels (1) and (2) in two stages with the chemical compositions of the fuels determined by the coefficients $\alpha = 1.4–1.9$, $\psi = 5–20$, and $\alpha_2 = 20$. The pressure in the combustion chamber and the initial pressure in the pressure chamber, where the active medium generator was located, remained unchanged and equal to 0.1 MPa and 0.1 kPa, respectively. The reproducibility of the experiments was ensured by three-regime launches, in which the first and third regimes corresponded to the reference experiment using molecular fluorine as an oxidiser, while the second regime, to the experiment using either nitrogen trifluoride or tetrafluorohydrazine. The power of laser radiation was measured according to the method of work [16] using a stable two-mirror closed-type optical cavity formed by an uncooled spherical mirror calorimeter with a diameter of 60 mm and a curvature radius of 5 m, made of polished BRX-0.8 bronze. The position of the resonator's optical axis x_c relative to the nozzle block cut-off was considered optimal from the viewpoint of attaining the maximum specific energy output: the parameter x_c^{opt} was 28 mm for the $N_2F_4–D_2–He$ fuel and 20 mm for the $NF_3–D_2–He$ fuel. For the ignition of NF_3, a chemical ignition method was used as the simplest and most reliable. It consisted in feeding molecular fluorine into the generator's combustion chamber for the start-up period (up to 0.5 s), followed by its gradual replacement with NF_3. As for the N_2F_4 fuel, it reliably self-ignited upon contact with D_2 in all tests.

5. Results of computational and experimental research

The energy advantages of the $N_2F_4–D_2–He$ fuel are due to a larger thermal effect of the reaction of tetrafluorohydrazine with deuterium, which allows increasing the mass yield of atomic fluorine. This follows from the results of thermodynamic calculations performed for adiabatic combustion conditions in a wide range of variations in the coefficients α and ψ ($\alpha = 1.4–2.0$ and $\psi = 5–20$ at $p_c = 0.1$ MPa). In addition to an increase in the atomic fluorine concentration, an increase in the temperature in the combustion chamber of the atomic fluorine generator when using N_2F_4 leads to an increase in the mixture temperature at the outlet of the oxidising gas nozzles. Despite the increase in molecular mass, this accelerates the diffusion of the jets of the oxidising gas (F – DF – He – N_2 mixture) and secondary fuel (H_2) in the resonator cavity (laser chamber) and, thereby, improves the energy characteristics of the HF laser.

Figures 1 and 2 show the calculated dependences of the specific energy output N_Σ on the coefficients α and ψ when the HF laser operates on the $NF_3–D_2–He$ and $N_2F_4–D_2–He$ fuels. The dependences $N_\Sigma = f(\psi)$ at $\alpha = \text{const}$ and $N_\Sigma = f(\alpha)$ at $\psi = \text{const}$ for both fuels have clearly expressed maxima. Their origin can be explained as follows.

At $\alpha = \text{const}$ (Figs 1a and 2a) and small values of the dilution coefficient ψ, heat release in the pump reaction $F + H_2 \rightarrow HF(v) + H$ leads to a sharp increase in the temperature of the active medium. This reduces both the lasing zone length and the efficiency of converting the chemical energy of the fuel into the energy of coherent radiation, which is characterised by the specific power value per unit mass flow rate of free atomic fluorine N_F. As a result, the specific energy output N_Σ is also reduced. At too high values of ψ, the increase in the specific power N_F can no longer compensate for a decrease in the content of fluorine atoms in the flow with an increase in the ψ coefficient due to both the recombination of atoms and a decrease in their proportion caused by dilution. The latter circumstance leads to a decrease in N_Σ.

In the case $\psi = \text{const}$ (Figs 1b and 2b), a decrease in the specific energy output N_Σ at low α values is due to the insignificant content of fluorine atoms in the combustion products

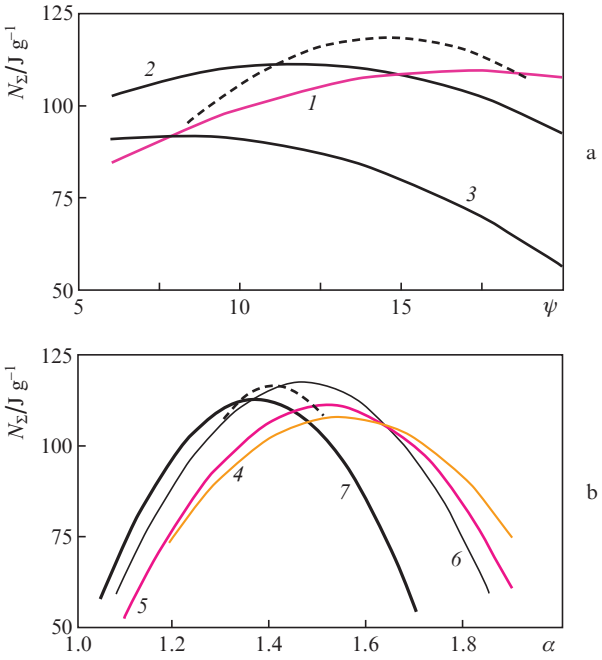

Figure 1. Calculated dependences of the HF-CWCL specific energy output on (a) the dilution coefficients and (b) the oxidiser excess when using $NF_3–D_2–He$ fuel: α = (*1*) 1.3, (*2*) 1.5, and (*3*) 1.7; ψ = (*4*) 8, (*5*) 10, (*6*) 15, and (*7*) 20.

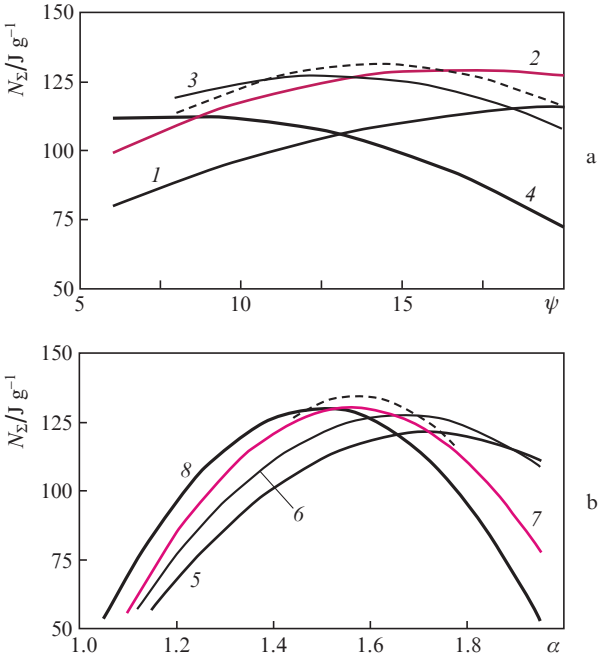

Figure 2. Calculated dependences of the HF-CWCL specific energy output on (a) the dilution coefficients and (b) the oxidiser excess when using $N_2F_4–D_2–He$ fuel: α = (*1*) 1.3, (*2*) 1.5, (*3*) 1.7, and (*4*) 1.9; ψ = (*5*) 8, (*6*) 10, (*7*) 15, and (*8*) 20.

and the high content of DF molecules in these products, which are active relaxants of emitting HF(v) molecules. At large values of the coefficient α, a decrease in the specific energy output is caused by a decrease in the oxidiser dissociation degree in the combustion chamber of the atomic fluorine generator.

The presence of maxima in the dependences $N_\Sigma = f(\alpha)$ and $N_\Sigma = f(\psi)$ allows us to determine their optimal values corresponding to the maximum specific energy output $N_\Sigma^{\max}$. To do this, envelopes, i.e. 'optimal' curves (dashed lines), are drawn through the maximum points of each family of curves $N_\Sigma = f(\psi)$ at α = const (Figs 1a and 2a) and $N_\Sigma = f(\alpha)$ at ψ = const (Figs 1b and 2b), which determine the values of $\alpha_{\rm opt}$ and $\psi_{\rm opt}$ (optimal chemical composition of NF_3-D_2-He and $N_2F_4-D_2-He$ fuels). Similar families of curves were obtained experimentally.

These coefficients were as follows: $\alpha_{\rm opt}^{\rm theor}/\alpha_{\rm opt}^{\rm exp} = 1.43/1.44$, $\psi_{\rm opt}^{\rm theor}/\psi_{\rm opt}^{\rm exp} = 13.0/11.6$ (for the NF_3-D_2-He fuel) and $\alpha_{\rm opt}^{\rm theor}/\alpha_{\rm opt}^{\rm exp} = 1.62/1.59$, $\psi_{\rm opt}^{\rm theor}/\psi_{\rm opt}^{\rm exp} = 15/12$ (for the $N_2F_4-D_2-He$ fuel). It can be seen that the accuracy of the numerical evaluation of the optimal chemical compositions of fuels is quite high. The calculated values of the maximum specific energy output virtually coincide with the results of experiments: for the NF_3-D_2-He fuel, the calculated value of $N_\Sigma^{\max}$ is 117 J g^{-1}, while its corresponding experimental value is 100 J g^{-1}; for the $N_2F_4-D_2-He$ fuel, these values constitute 134 and 113 J g^{-1}, respectively.

The data presented allow us to directly compare the specific energy output of an HF laser operating with fuels with different oxidisers. This comparison shows that the replacement of nitrogen trifluoride with tetrafluorohydrazine in the studied laser model with a nozzle block corresponding to the nozzle–nozzle reagent mixing scheme leads to an increase in N_Σ by 13%–15%.

A similar ratio of specific energy outputs was obtained in work [7] when working with N_2F_4 and NF_3 fuels (an increase of up to 13% with the N_2F_4 fuel) on an experimental model of the HF laser with a power of less than 1 kW, having a nozzle block of a fundamentally different design with a size of 150 × 33 mm, based on a single nozzle corresponding to a hypersonic low-temperature flow scheme.

On the one hand, such an increase should be considered quite moderate. But, on the other hand, as noted above, attention to the use of nitrogen fluorides as oxidisers in supersonic HF-CWCLs is mainly due to their operational advantages. Since the assessment of the possible effect of their implementation is of certain interest, a comparative analysis has been performed of the mass and size characteristics of the oxidiser storage system of a laser facility based on a high-power HF laser operating with two types of oxidisers, i.e. nitrogen trifluoride and tetrafluorohydrazine.

6. Comparative evaluation of the mass and size characteristics of the oxidiser storage system of a high-power HF laser

For definiteness, we consider a facility with a lasing power level of N = 100 kW and a continuous operation duration of τ = 100 s. The initial data for the calculation were taken with allowance for the results of the computational and experimental study (Section 5). To simplify the calculations, only the oxidiser and storage tank masses were taken into account as part of the oxidiser storage system. The oxidiser mass was determined with regard to the optimal chemical composition of the fuel (coefficients $\alpha_{\rm opt}$ and $\psi_{\rm opt}$), the level of laser output power N, the duration of its operation τ and the total consumption of the fuel mixture $m_\Sigma = N/N_\Sigma^{\max}$.

The oxidiser storage tanks were ball cylinders. The accepted storage conditions for oxidisers in tanks are presented in Table 1. The calculation of the ball cylinder's mass was reduced to determining its volume, inner diameter, and wall thickness. For these calculations, the following parameters were adopted: the cylinder material was stainless steel with a specific mass of 7920 kg m^{-3}, the maximum stress of the material was taken equal to 530 MPa, the material safety factor was 2, and the filling factor of the cylinder with a liquid product (tetrafluorohydrazine) was 0.8.

Table 1. Storage conditions for oxidisers in the fuel tanks of the laser facility.

Oxidiser type	Tank presure/ MPa	Tank component temperature/K	Tank component density/ kg m^{-3}	Aggregate state
NF_3	15.0	293	418.6	Gas
N_2F_4	2.5	293	1454.0	Liquid

Calculations of the specific mass M/N of the oxidiser storage system (M is the oxidiser storage system's mass) have shown that the implementation of the operational advantages of tetrafluorohydrazine reduces the specific mass of its storage system by three times (0.8 kg kW^{-1}) compared to the specific mass of the nitrogen trifluoride storage system (2.5 kg kW^{-1}). The relative simplicity of converting tetrafluorohydrazine to a liquid state and storing it in this state without forced cooling allows reducing the volume and, accordingly, the overall dimensions of the oxidiser tank. Indeed, the diameter of the tank with N_2F_4 fuel (0.6 m) turned out to be 1.7 times smaller than the diameter of the tank with NF_3 fuel (1.0 m).

Thus, the results of this work have shown that the replacement of nitrogen trifluoride with tetrafluorohydrazine in the NF_3-D_2-He fuel for the atomic fluorine generator of a supersonic cw chemical HF laser makes it possible to increase its specific energy output by 13%–15%, to reduce the specific mass of the oxidiser storage system and the overall oxidiser tank dimensions, and also to simplify the design of the active medium generator by eliminating the ignition system of the NF_3 oxidiser in contact with the primary D_2 fuel. These advantages can be realised regardless of the nozzle block design. As for the availability of tetrafluorohydrazine, a technical product with a 96% volume content of N_2F_4 was being produced in the United States in the 1990s. Its cost was $200 per kilogram. This product is not produced in Russia.

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